

**Project Title:** Measuring the Optical Properties and Climate Impacts of Aerosol from Wild and Prescribed Fires in the US

**Final Report:** JFSP Project Number 11-1-5-12

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This research was sponsored by the Joint Fire Science Program. For further information go to [www.firescience.gov](http://www.firescience.gov).



## I. Abstract

This project characterized the emissions from a simulated wildfire and their evolution downwind via an airborne platform hosting state of the science online measurement techniques for speciated PM<sub>1</sub> aerosol, black carbon, water soluble particulate organic carbon, and levoglucosan, a smoke marker compound. Our project leveraged resources provided by a larger study funded by SERDP, that supported the flight hours for the airborne platform (USFS Twin Otter) and also supported complementary observations of trace gas emission factors, plume heights, meteorological data, and fuel consumption. The field study took place in October-November 2011 in South Carolina. The prescribed burns that were sampled were conducted at the U.S. Army's Fort Jackson. Fuels burned were primarily from the pine-forest understory in relatively dense longleaf pine stands that had not been disturbed by fire in over 50 years. We also sampled additional fires of opportunity.

Four major sets of findings have resulted from this project to date, as follows.

(1) In our field study, 97 trace gases were quantified in the emissions, representing one of the most comprehensive fire emissions databases to date (Akagi et al., 2013). For the first time, a suite of monoterpenes was measured, representing compounds released from the heating of fuels prior to ignition. Significant ozone production was measured in all of the sampled plumes, indicative of vigorous photochemistry.

(2) We combined the black carbon measurements from this study with those from a number of previous field studies and compared them to laboratory-derived emission factors, sorted by modified combustion efficiencies (May et al., 2014). The lab and field data for black carbon compared well, giving confidence in the utility of lab studies for determining emissions factors; however, measurements made using a new real-time instrument, the Single-Particle Soot Photometer, were higher than earlier measurements based on filter samples, suggesting upward revision may be needed for currently-applied black carbon emission factors. The laboratory data for emission factors of organic carbon aerosol were higher than the field data suggested. This finding was likely due at least in part to the greater dilutions encountered in the atmosphere and the subsequent evaporation of organic aerosol, demonstrating that the semivolatile nature of biomass burning aerosol emissions must be taken into account in emissions and transport modeling.

(3) Semi-continuous measurements of water-soluble organic carbon clearly indicated plume penetrations, supported by the first reported airborne time-resolved smoke marker concentrations (Sullivan et al., 2014). Smoke marker ratios obtained in the airborne sampling were consistent with those obtained in the laboratory, further confirming the utility of lab studies for emissions characterization. The aircraft data indicated that the ratio of levoglucosan to water-soluble organic carbon was a stable tracer ratio for at least 1.5h of plume aging.

(4) For the Fort Jackson prescribed burns, speciated particulate matter measurements at the fire and following the plume downwind showed a net loss of organic aerosol, particularly in the first 1.5h. Evolution of the composition of the organic aerosol was also observed, including an apparent increase in the degree of oxygenation. Although we could not rule out

photochemical processes as drivers of the observed changes, we found the changes in the in-plume organic aerosol were consistent with a primarily physical evolution of the emissions, namely, volatilization of organic aerosol compounds upon dilution with background air (May et al., in prep).



Image taken from onboard the airborne laboratory, of the plume from a Ft. Jackson prescribed burn during SCREAM (South Carolina Regional Emissions and Aging Measurements).

## II. Background and Purpose

Although representing only a small mass fraction of the emissions from biomass burning, black carbon (BC) exerts a strong influence on climate. As a component of the atmospheric aerosol, BC absorbs visible light and warms the adjacent air, potentially altering the vertical temperature profile. If deposited to bright surfaces such as snow, BC may accelerate melting. Biomass burning is a large, but highly variable, global source of BC. Biomass burning emissions of BC are strongly correlated with increased flaming to smoldering ratios and likely correlated with increased combustion intensity, but these effects still need better quantification. A critical issue is that nearly all of the BC emitted by flaming combustion of biomass is found in particles that also contain much larger amounts of organic aerosol (OA) from smoldering combustion. The OA in the particles contributes to atmospheric cooling both directly, by reflecting solar radiation, and indirectly, by serving as cloud condensation nuclei that cause clouds to reflect more solar radiation. The increased solubility of particles containing water-soluble OA makes them more likely to serve as cloud condensation nuclei and to be removed from the atmosphere by rainfall, limiting their atmospheric lifetimes and impacts on radiation budgets. Because of the co-emitted OA, biomass burning BC likely contributes less to global warming than an equal amount of BC emitted by fossil fuel combustion. In fact, aerosols from biomass burning are thought to have an overall cooling effect on climate, mitigating the warming associated with BC from that source. Further, it is possible that differences in the BC/OA ratio for wild and prescribed fires could lead to different climate impacts. Any assessment of the climate impacts of biomass burning BC must consider the co-emitted OA.

A major barrier to quantifying the climate impact of BC and OA emitted by wild and prescribed fires is that the traditional measurement methods for both BC and OA are filter-based and suffer from poor time resolution and numerous artifacts. In this study, we measured the BC and OA emitted by the combustion of biomass with new, more accurate technology as part of an airborne platform that sampled smoke from several simulated wild fires at Fort Jackson, SC in October-November 2011. The simulated wildfires were prescribed fires in unusually heavy fuel loads in long leaf pine stands. The airborne laboratory, already funded separately by SERDP, was augmented through this project with a soot photometer (SP2), a high-resolution aerosol mass spectrometer (HR-AMS), and a particle-into-liquid sampler (PILS). This suite of aerosol instrumentation obtained accurate, high-time-resolution emission factor measurements for BC, OA, water soluble OA, and key smoke marker molecules. Ozone and a large suite of trace gases were also measured from this platform, permitting estimates of trace species emissions factors (EFs) as functions of modified combustion efficiency. Further, we employed a Lagrangian sampling strategy that characterized the evolution of the emissions downwind, to obtain information on how the emissions evolved with plume dilution and photochemical aging.

Through this field study and the subsequent analyses, we pursued the following project objectives:

1. Complete the first field measurements with advanced, accurate instrumentation for determination of EFBC, EFOA, and EFWSOC for simulated wildfires and prescribed fires in the SE US (near Columbia, South Carolina).
2. Compile recent observations of EFBC to update existing inventories.
3. Measure smoke markers in the sampled emissions from the airborne laboratory, using a new time-resolved technique, and compare with smoke marker ratios measured in laboratory studies.
4. Examine the atmospheric stability of the smoke marker levoglucosan.
5. Examine the evolution of OA emissions in the diluting plume, including evolution of OA chemical composition.
6. Effectively disseminate project findings to those involved in fire management, air quality analysis, and modeling of smoke impacts.

### III. Study Description

#### *Aircraft operations*

The field study (SCREAM: South Carolina Regional Emissions and Aging Measurements) was conducted in late October – early November 2011 in the Sandhills region of South Carolina. The project team and aircraft were based out of Columbia, and the prescribed burns that were undertaken specifically for this project were conducted at the US Army’s Fort Jackson base. Since a primary goal of this work was to look at the differences in emissions between typical prescribed burns and wildfires, the site selected was based on the availability of several longleaf pine stands that had not been logged or burned by wild or prescribed fires in over 50 years, and thus had a dense understory. Further, the understory fuels had more hardwoods, litter and shrubs than would typically be combusted during a prescribed burn in a more regularly managed stand. The fire was ignited in a manner intended to create an intense burn simulating a small wildfire. Fuels characterizations were conducted prior to the burns and ground-based sampling of emissions was also performed; sampling of trace gases and meteorological data was conducted from the airborne observational platform. These data were used in our analyses and reported in the resulting publications, but here we report on the specific airborne aerosol measurements that were supported by this project.

The airborne sampling strategy was to begin operations within about an hour of ignition, repeatedly sampling the emissions and the background near the source in order to develop a robust picture of the variability in the emissions factors and in the combustion conditions as represented by the modified combustion efficiencies. The pilot then used prevailing wind data and real-time onboard observations to follow the plume downwind as it diluted and aged (e.g., Fig. 1). A second flight was undertaken in the afternoon, in which the aircraft returned to the

source to characterize emissions at a later stage in the burn and then repeated downwind sampling.

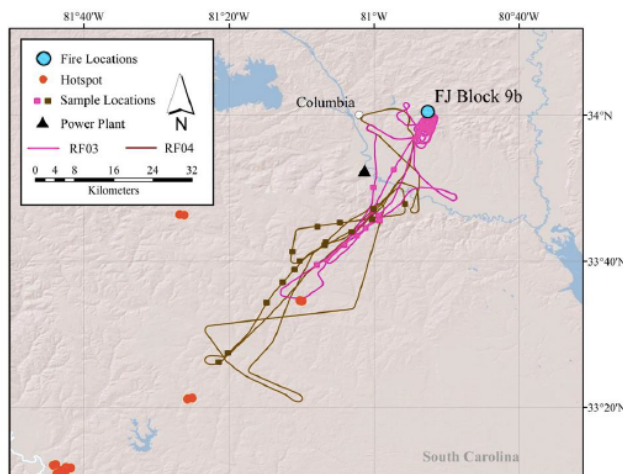


Figure 1 (from Akagi et al., 2013). Flight tracks during RF03 (pink) and RF04 (brown), which sampled the Block 9b fire at Fort Jackson on 1 November 2011.

The Fort Jackson burns were concluded on November 2. The remaining available flight hours were used to sample urban background air (5 November) and fires of opportunity in the region (7-10 November), in some cases permitting both source characterization and plume evolution sampling. Table 1 provides a summary of the flights conducted during SCREAM.

#### *Aerosol measurements (further details provided in associated publications)*

**Inlet.** All aircraft aerosol measurements were made for the PM<sub>1</sub> aerosol fraction. The PM<sub>1</sub> cutpoint was achieved via sampling from a low turbulence inlet followed by a nonrotating MOUDI impactor with a 50% transmission efficiency at 1  $\mu\text{m}$  and 1 atm ambient pressure. The combined flow through the inlet and MOUDI, approximately 20 L min<sup>-1</sup>, was split to the individual instruments.

**SP2 (single-particle soot photometer).** The SP2 provided real-time observations of black carbon particle mass distributions at 1 s resolution. The operating principle involves illuminating particles with laser light tuned to a strongly absorbing peak in black carbon. Black carbon particles absorb the light, incandesce, and vaporize; the incandescence signal is calibrated to black carbon mass via lab standards.

**HR-AMS (high-resolution aerosol time-of-flight mass spectrometer).** The HR-AMS measured the nonrefractory aerosol components at 6 s resolution. These were reported as total PM<sub>1</sub> organic aerosol, sulfate, nitrate, and ammonium (other species are too low for reliable detection). Particles are impacted onto a heater and vaporized and ionized, with the resulting

mass fragments detected by the mass spectrometer. Calibrations were performed with ammonium sulfate aerosol periodically throughout the study.

**WSOC (water-soluble organic carbon), K<sup>+</sup> (water-soluble potassium), and LEV (levoglucosan).** A PILS (Particle-into-Liquid Sampler) was used to collect ambient particles into purified water, providing a semi-continuous stream of liquid sample for analysis. A portion of the sample was sent to a Total Carbon Analyzer to detect the total dissolved organic carbon, which was taken as the WSOC in the aerosol, at 3 s time resolution. The remaining sample was sent to a fraction collector that accumulated 2 min aliquots, which were subsequently analyzed in the CSU laboratory for water-soluble potassium and levoglucosan and other carbohydrates.

**Trace gases.** CO<sub>2</sub>, CO, CH<sub>4</sub>, and water vapor mixing ratios were measured by a cavity ring-down spectrometer, calibrated in-flight with mixed CO/CO<sub>2</sub>/CH<sub>4</sub> standards. (These data were obtained by our research partner S. Urbanski.)

Table 1. Summary of flights in the SCREAM campaign. Color coding represents the following: grey: no fire sampling. Yellow through red: fire emissions sampling, with relative fire intensities indicated by the depth of the color.

<i>Date</i>	<i>Flight Name</i>	<i>Wheels up</i>	<i>Wheels down</i>	<i>Purpose / Mission Summary</i>	<i>Notes</i>
(2011)		LT (EDT/EST)	LT (EDT/EST)		
27-Oct	Test Flight 1 (TF01)			Near Broomfield, CO	
29-Oct	TF02			Near Columbia, SC	
30-Oct	Research Flight 1 (RF01)	1235	1406	Block 6 Fire Fort Jackson (source and downwind (attempt))	least intense of FJ fires (all FJ fires more intense than non-FJ fires)
30-Oct	RF02	1449	1710	Block 6 Fire Fort Jackson (source and downwind (attempt))	least intense of FJ fires (all FJ fires more intense than non-FJ fires)
31-Oct	No Flight				
1-Nov	RF03	1156	1452	Block 9 Fire Fort Jackson (source and downwind)	no communications with ground on this flight
1-Nov	RF04	1604	1746	Block 9 Fire Fort Jackson (source and downwind)	second most intense fire, peak during re-fuel
2-Nov	RF05	1258	1658	Block 8 (22B) Fire Fort Jackson (source and downwind (attempt))	most intense fire + landfill emissions
3-Nov	No Flight				pilot days off
4-Nov	No Flight				pilot days off
5-Nov	RF06	~1030	1121	Circle Columbia Metro Area for deconvoluting urban/fire sources	Allow for weekend effect
6-Nov	No Flight				<i>DST ends EDT&gt;EST</i>
7-Nov	RF07	1238	1508	2-3 fires along coast (one at source and downwind)	(1) hazard reduction in loblolly (understory), (2) grass fire, (3?) possible trash fire in mix
8-Nov	RF08	1247	1538	Fire on Francis Marion NF (source and downwind)	hazard reduction in loblolly (understory)
9-Nov	No Flight				
10-Nov	RF09	1151	1359	Bamberg Fire	7-8 fires in all

### *Background corrections*

Plume penetrations and background air samples were defined via inspection of the data. Background data were averaged before and after plume crossings and then subtracted from in-plume observations to obtain excess concentrations due to the emissions. In-plume measurements were integrated across the plume. Data were generally reported as the ratio of the excess species concentration to the excess carbon monoxide concentration, thus correcting for plume dilution.

## **IV. Key Findings**

The key findings section provides a brief summary of the results and key citations for each. More detailed descriptions of the methods and findings are available from the publications resulting from this work.

### **IV.a. Substantial ozone production occurred in fresh smoke plumes within 2 hours of emission**

Emissions from fires are diluted as they are transported downwind, and evolve chemically and physically upon exposure to sunlight, other pollutants, and oxidants such as ozone ( $O_3$ ), hydroxyl radicals (OH), and nitrate ( $NO_3$ ) radicals. An improved understanding of the contributions of biomass burning emissions to local and regional photochemistry is required to quantify the impacts of prescribed and wild fires on air quality and potential violations of standards. SCREAM was part of an ongoing series of experiments to examine the impacts of fire emissions on ozone formation, focusing on the evolution of ozone within smoke plumes. The environment in SCREAM was such that dilution occurred very rapidly, and in some of the cases, emissions were quickly mixed with the  $NO_x$ -rich urban plume from Columbia, SC. Although  $\Delta O_3/\Delta CO$  was highly variable burn to burn, the SCREAM data included the fastest ozone formation rates thus far reported, likely due to these interactions with urban emissions that shifted the chemistry away from a  $NO_x$ -limited regime. Figure 2 compares the SCREAM data to two prior studies and shows a similarity with observations in Mexico, supporting earlier conclusions that ozone production is favored in tropical plumes.

SCREAM featured quantified emissions estimates for an unprecedented 97 trace gases, including a suite of monoterpenes emitted during pre-combustion heating of the fuels. Since monoterpenes are known to react quickly in the atmosphere with ozone to produce secondary organic aerosols, their quantification enabled for the first time data-based estimates of their impacts on both net ozone formation and secondary organic aerosol formation.

Tabulations of emission factor data are provided in the publication.

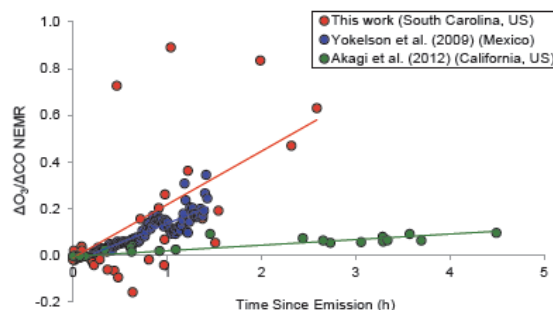


Figure 2 (from Akagi et al., 2013).  $\Delta\text{O}_3/\Delta\text{CO}$  as a function of time since emission for the SCREAM study (red points and line) compared with selected previously-reported observations.

Key publication:

Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreidenweis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R. (2013), Measurements of reactive trace gases and variable  $\text{O}_3$  formation rates in some South Carolina biomass burning plumes, *Atmos. Chem. Phys.*, 13, 1141-1165, doi:10.5194/acp-13-1141-2013.

#### IV.b. Aerosol species emission factors from lab and field work are in reasonable agreement, except for organic carbon

We compiled aerosol-phase species emissions data from several prior lab studies and field campaigns, including SCREAM, using MCE and fuel type as the discriminating variables (Fig. 3). We concluded that lab and field data were in reasonable agreement for most of the fuels tested, as shown in Fig. 4 for black carbon. A prominent exception was for organic carbon aerosol (Fig. 3b), with estimated emission factors derived from laboratory data consistently and significantly higher than those from field observations. We attributed this bias to the lower dilutions and higher mass concentrations in the laboratory observations, and secondarily to other factors such as fuel moisture and type. The differences in the two sets of OA observations thus point to the need for a treatment of organic aerosol emissions that considers their volatility distributions in addition to quantifying the total emissions of “potential OA” species up to high-volatility compounds.

We also confirmed that the emissions of nonrefractory inorganic aerosol species were dependent on fuel type in addition to MCE (Figs. 3c,d,e,f). In particular, grasses had high emissions of chloride, reflective of their composition which tends to be higher in chlorine and potassium than other fuels.

## Key publication:

May, A. A., G. R. McMeeking, T. Lee, J. W. Taylor, J. S. Craven, I. Burling, A. P. Sullivan, S. Akagi, J. L. Collett Jr., M. Flynn, H. Coe, S. P. Urbanski, J. H. Seinfeld, R. J. Yokelson, and S. M. Kreidenweis (2014), Aerosol emissions from prescribed fires in the United States: A synthesis of laboratory and aircraft measurements, *J. Geophys. Res. Atmos.*, 119, doi:10.1002/2014JD021848.

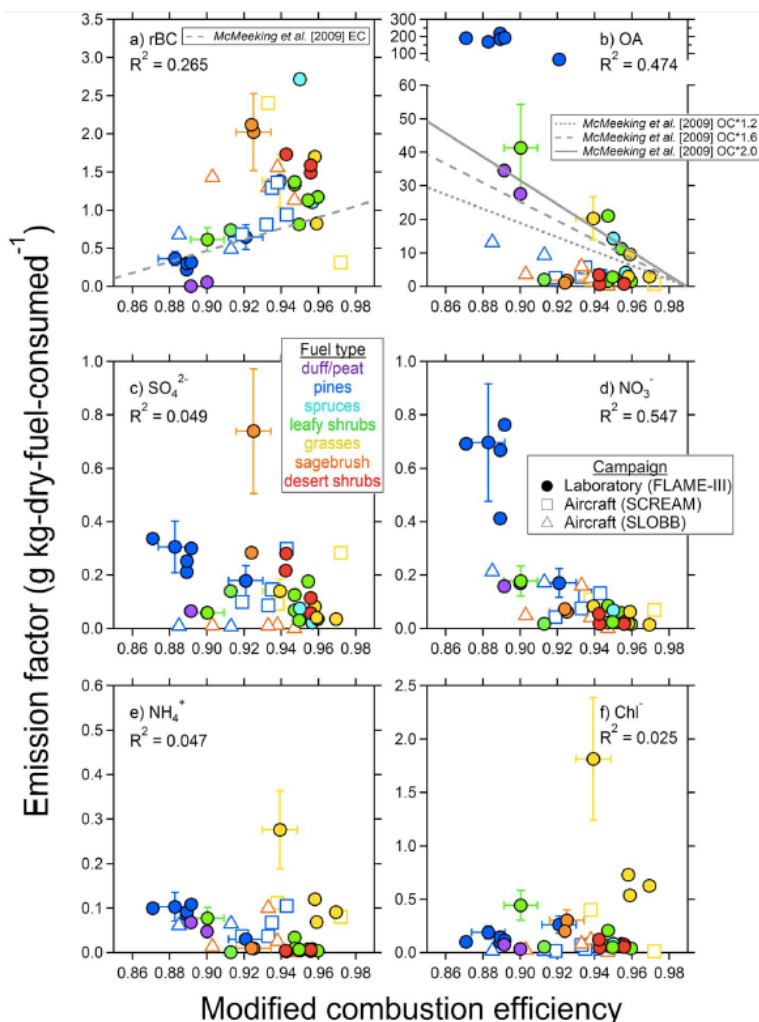


Figure 3 (from May et al., 2014). Emission factors of various aerosol-phase species as shown in legends. Points are colored according to approximate fuel classification. Open points: field studies. Closed points: lab studies. Dashed line in (a) corresponds to relationship proposed by McMeeking et al. (2009), using filter-based measurements of black carbon. (McMeeking, G. R., S. M. Kreidenweis, S. Baker, C. M. Carrico, J. C. Chow, J. L. Collett, W. M. Hao, A. S. Holden, T. W. Kirchstetter, et al., Emissions of trace gases and aerosols during the open combustion of biomass in the laboratory. *Journal of Geophysical Research-Atmospheres* **114**, D19210, 10.1029/2009jd011836, 2009.)

#### IV.c. Emission factors for black carbon are higher based on new online measurement methods, relative to existing filter-based estimates

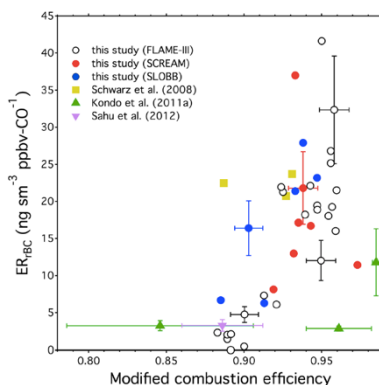


Figure 4 (from May et al., 2014). Emission ratios for black carbon from field observations (solid points) and lab data (open points). All studies shown used the SP2 instrument to quantify black carbon mass concentrations. Kondo et al. data are for plumes sampled after several days of long range transport.

Figure 4 shows a comparison of our lab and field data for black carbon emissions ratios from SP2 measurements, along with prior field measurements using the same instrument. There was good agreement when data were sorted by MCE, with the possible exception of one study that intercepted very aged plumes; we speculate that washout of black carbon occurred during the long range transport of those emissions, resulting in lower apparent emission ratios. Fig. 4 contrasts with the dashed line in Fig. 3a, which represents the emission factor as a function of MCE derived in earlier lab studies using filter-based methods. Many of the SP2 data deviated by more than a standard deviation from the older data. We suggest that emission factors for black carbon may require upward revision, pending further experimental confirmation that SP2 measurements capture the true mass concentrations of black carbon better than did prior filter-based measurements, known to be subject to analysis artifacts.

##### Key publication:

May, A. A., G. R. McMeeking, T. Lee, J. W. Taylor, J. S. Craven, I. Burling, A. P. Sullivan, S. Akagi, J. L. Collett Jr., M. Flynn, H. Coe, S. P. Urbanski, J. H. Seinfeld, R. J. Yokelson, and S. M. Kreidenweis (2014), Aerosol emissions from prescribed fires in the United States: A synthesis of laboratory and aircraft measurements, *J. Geophys. Res. Atmos.*, 119, doi:10.1002/2014JD021848.

#### IV.d. The ratio of the excess primary smoke marker levoglucosan to excess water-soluble organic carbon aerosol is stable for at least 1.5h of plume aging

Levoglucosan (1,6-anhydro- $\beta$ -D-glucopyranose) is an important marker for source apportionment of biomass burning. Source apportionment analyses currently assume that levoglucosan is conserved in the atmosphere. However, recent laboratory work has shown that levoglucosan is subject to chemical degradation in the atmosphere, with a measured lifetime of

0.7-2.2 days. Our in situ observational strategy permitted the first in-plume study of levoglucosan stability; results are shown in Fig. 5. Over the time frame shown, approximately 1.5h after emission, there is no evidence of a change in the ratio of  $\Delta\text{LEV}$  to  $\Delta\text{WSOC}$ , suggesting characteristic ratios for emissions can be used for source apportionment of WSOC.

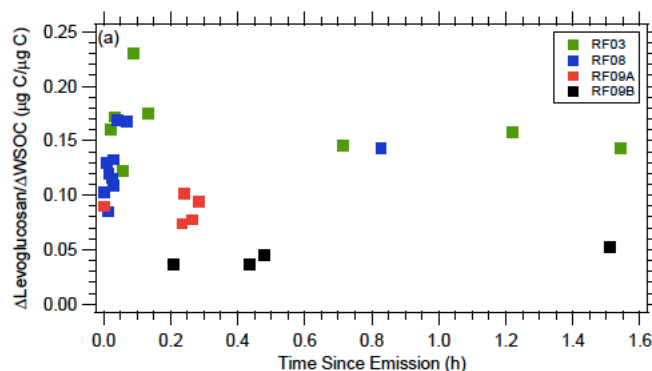


Figure 5 (from Sullivan et al., 2014). Ratios of excess levoglucosan to excess water-soluble organic carbon, as a function of time since emission.

Key publication:

Sullivan, A. P., May, A. A., Lee, T., McMeeking, G. R., Kreidenweis, S. M., Akagi, S. K., Yokelson, R. J., Urbanski, S. P., and Collett Jr., J. L. (2014), Airborne characterization of smoke marker ratios from prescribed burning, *Atmos. Chem. Phys.*, 14, 10535-10545, doi:10.5194/acp-14-10535-2014.

#### IV.e. The ratio of the excess primary smoke marker levoglucosan to excess water-soluble organic carbon aerosol is a function of fuel type and is well represented by laboratory data

As shown in Fig. 6, specific fuel categories – needles, grasses, leaves and marsh grasses – tend to have unique variations of the ratio  $\Delta\text{LEV}/\Delta\text{WSOC}$  with MCE, suggesting this characteristic can be exploited for source apportionment. Further, the ratios observed in SCREAM were consistent with those obtained from prior laboratory studies. We applied the lab-derived ratios to SCREAM data to determine that the emissions from the Fort Jackson burns were dominated by the burning of grasses, whereas the Frances Marion fire, set to reduce fire hazard in loblolly understory, appeared to burn primarily leaves. The  $\Delta\text{LEV}/\Delta\text{WSOC}$  measurements suggested that the Bamberg plume was actually from two different fires, one burning needles and the other marsh grasses; other measurements subsequently confirmed that the aircraft had sampled emissions from two different sources.

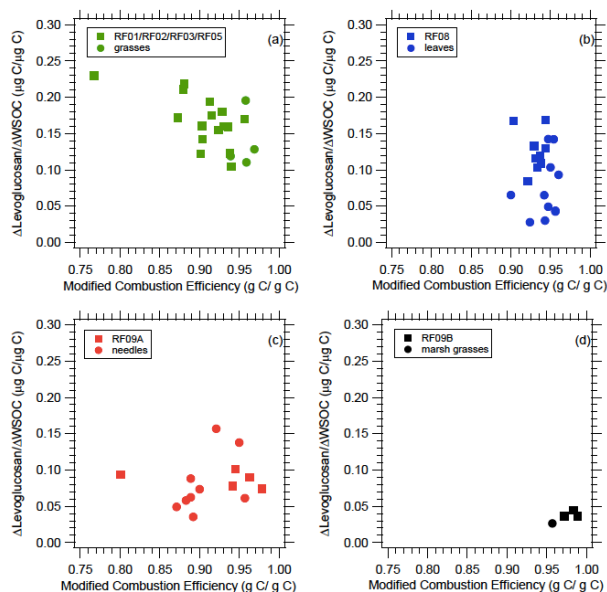


Figure 6 (from Sullivan et al., 2014). Ratios of excess levoglucosan to excess water-soluble organic carbon, as a function of fuel type (grasses, leaves, needles and marsh grasses). Laboratory and field study data are shown by circles and squares, respectively.

#### Key publication:

Sullivan, A. P., May, A. A., Lee, T., McMeeking, G. R., Kreidenweis, S. M., Akagi, S. K., Yokelson, R. J., Urbanski, S. P., and Collett Jr., J. L. (2014), Airborne characterization of smoke marker ratios from prescribed burning, *Atmos. Chem. Phys.*, 14, 10535-10545, doi:10.5194/acp-14-10535-2014.

#### IV.f. The volatilization of organic aerosol emitted by biomass burning upon dilution in the atmosphere was accompanied by apparent changes in chemical composition

Fig. 7 shows data from one of the SCREAM case studies, with all quantities shown as a function of time since emission (i.e., distance downwind). Emissions were diluted rapidly, on characteristic timescales of  $\sim 30$  min. While black carbon, an inert tracer, was reasonably well conserved, it is clear that a net loss of organic aerosol occurred within about 1.5h of emission. This net loss was due to the evaporation of semivolatile species and could be modeled using published volatility distributions for biomass burning emissions. Interestingly, as shown in the lower panels of Fig. 7, these physical changes to the emitted aerosol were accompanied by changes in observed chemical composition. The fragment  $m/z$  60 is closely correlated with levoglucosan concentrations and a decrease in its fractional contribution to excess organic aerosol was observed as dilution proceeds. At the same time,  $m/z$  44 increased its fractional contribution to the excess OA in the plume, suggesting the species contributing to this fragment are less volatile than those dominating the  $m/z$  60 signal. The  $m/z$  44 fragment is commonly

assumed to indicate degree of oxygenation; elemental ratio analyses confirmed that O:C increased with time since emission. Although these chemical changes could be indicative of active chemistry producing more-oxygenated secondary organic aerosol that partitions into the gas phase, offsetting some of the evaporation, similar changes in  $f_{60}$  and  $f_{44}$  have been observed in lab studies of only thermal processing of biomass burning emissions. Thus while our observations cannot rule out the possibility that oxygenated secondary organic aerosol was forming in the plume, the data are consistent with solely physical changes over the first few hours after emission that result in changes in chemical composition, namely, preferential evaporation of less-oxygenated species. The composition of the evaporated species is currently unknown. However, these species, once released to the gas phase, may play a role in the photochemistry producing ozone and SOA in biomass burning plumes. Thus future work is needed to identify these compounds and to assess their impacts on air quality.

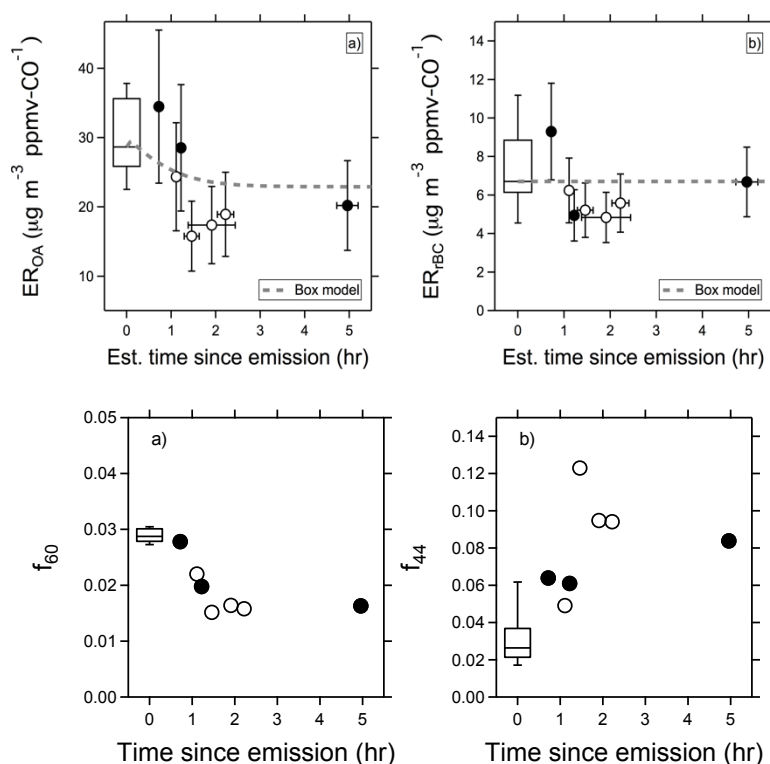


Figure 7 (from May et al., in prep). Measurements from the Fort Jackson Plot 9b burn. Upper panel: the emission ratios (excess species, ratioed to excess carbon monoxide) for (a) organic carbon aerosol and (b) black carbon, as functions of time since emission. Lower panel: the fraction of excess organic aerosol mass attributed to the fragments (a) m/z 60 and (b) m/z 44.

#### Key publication:

May, A. A., T. Lee, G.R. McMeeking, S. Akagi, A.P. Sullivan, S. Urbanski, R.J. Yokelson, and S.M. Kreidenweis, Investigation of Chemical and Physical Perturbations to Organic Aerosol Present in Biomass Burning Plumes over Prescribed Fires in South Carolina, *manuscript in preparation*.

#### IV.g. Outreach

As part of this project we conducted outreach by means of the participation and sharing of results at a number of conferences, workshops, and meetings; see partial list below.

##### IV.g.1. Publications: Peer-Reviewed Journal Articles

1. Akagi, S. K., Yokelson, R. J., Burling, I. R., Meinardi, S., Simpson, I., Blake, D. R., McMeeking, G. R., Sullivan, A., Lee, T., Kreidenweis, S., Urbanski, S., Reardon, J., Griffith, D. W. T., Johnson, T. J., and Weise, D. R. (2013), Measurements of reactive trace gases and variable O<sub>3</sub> formation rates in some South Carolina biomass burning plumes, *Atmos. Chem. Phys.*, *13*, 1141-1165, doi:10.5194/acp-13-1141-2013.
2. May, A. A., G. R. McMeeking, T. Lee, J. W. Taylor, J. S. Craven, I. Burling, A. P. Sullivan, S. Akagi, J. L. Collett Jr., M. Flynn, H. Coe, S. P. Urbanski, J. H. Seinfeld, R. J. Yokelson, and S. M. Kreidenweis (2014), Aerosol emissions from prescribed fires in the United States: A synthesis of laboratory and aircraft measurements, *J. Geophys. Res. Atmos.*, *119*, doi:10.1002/2014JD021848.
3. Sullivan, A. P., May, A. A., Lee, T., McMeeking, G. R., Kreidenweis, S. M., Akagi, S. K., Yokelson, R. J., Urbanski, S. P., and Collett Jr., J. L. (2014), Airborne characterization of smoke marker ratios from prescribed burning, *Atmos. Chem. Phys.*, *14*, 10535-10545, doi:10.5194/acp-14-10535-2014.
4. May, A. A., T. Lee, G.R. McMeeking, S. Akagi, A.P. Sullivan, S. Urbanski, R.J. Yokelson, and S.M. Kreidenweis, Investigation of Chemical and Physical Perturbations to Organic Aerosol Present in Biomass Burning Plumes over Prescribed Fires in South Carolina, *manuscript in preparation*.

##### IV.g.2. Conference Presentations

1. **Black Carbon Emissions from Prescribed Forest Fires in the Southeast United States.** Presented at the 32 Annual Conference of the American Association for Aerosol Research, September 30-October 4, 2103, Portland, Oregon. Authors: Amara Holder<sup>1</sup>, Gayle Hagler<sup>1</sup>, Gavin McMeeking<sup>2</sup>, Johanna Aurell<sup>3</sup>, Michael Hays<sup>1</sup>, Amy Sullivan<sup>5</sup>, Taehyoung Lee<sup>4</sup>, Shawn Urbanski<sup>6</sup>, Robert Yokelson<sup>7</sup>, Sonia Kreidenweis<sup>5</sup>, Brian Gullett<sup>1</sup> (<sup>1</sup>US Environmental Protection Agency; <sup>2</sup>Droplet Measurement Technologies; <sup>3</sup>University of Dayton; <sup>4</sup>Hankuk University of Foreign Studies, South Korea; <sup>5</sup>Colorado State University; <sup>6</sup>US Forest Service; <sup>7</sup>University of Montana)
2. **Examination of Airborne-Based Smoke Marker Ratios from Prescribed Burning.** Presented at at the 32 Annual Conference of the American Association for Aerosol Research,

September 30-October 4, 2103, Portland, Oregon. Authors: A.P. Sullivan<sup>1</sup>, A.A. May<sup>1</sup>, T. Lee<sup>2</sup>, G.R. McMeeking<sup>3</sup>, S.M. Kreidenweis<sup>1</sup>, S.K. Akagi<sup>4</sup>, R.J. Yokelson<sup>4</sup>, S.P. Urbanski<sup>5</sup>, and J.L. Collett, Jr. <sup>1</sup> (<sup>1</sup> Colorado State University; <sup>2</sup>Hankuk University of Foreign Studies, South Korea; <sup>3</sup>Droplet Measurement Technologies; <sup>4</sup>University of Montana; <sup>5</sup>US Forest Service)

3. **Biomass burning plume evolution during prescribed burns in South Carolina.** Presented at the Young Scientist Symposium on Atmospheric Research, September 20, 2013, Fort Collins, Colorado. Authors: A.A. May<sup>1</sup>, T. Lee<sup>1,2</sup>, S.K. Akagi<sup>3</sup>, A.P. Sullivan<sup>1</sup>, G. R. McMeeking<sup>1,4</sup>, S. Urbanski<sup>5</sup>, R. J. Yokelson<sup>3</sup>, S. M. Kreidenweis<sup>1</sup>. (<sup>1</sup>Colorado Sate University, Department of Atmospheric Science, Fort Collins, CO 80523; <sup>2</sup>Now with Hankuk University of Foreign Studies, Yongin, South Korea; <sup>3</sup>University of Montana, Department of Chemistry, Missoula, MT 59812; <sup>4</sup>Now with Droplet Measurement Technologies, Boulder, CO 80301; <sup>5</sup>USDA Forest Service, Rocky Mountain Research Station, Fire Sciences Laboratory, Missoula, MT 59808)
4. **Smoke as a Source of Terpenes, Hemi-terpenes and OVOCs.** Presented at the International Smoke Symposium of the International Association of Wildland Fire, October 21-14, 2013, Adelphi, MD. Authors: Sheryl Akagi<sup>1</sup>, Ian R. Burling<sup>1</sup>, Robert J. Yokelson<sup>1</sup>, Timothy J. Johnson<sup>2</sup>, Albert Mendoza<sup>2</sup>, David R. Weise<sup>3</sup>, James Reardon<sup>3</sup>, and Shawn Urbanski<sup>3</sup>, Gavin R. McMeeking<sup>4</sup>, Hugh Coe<sup>5</sup>, Taehyoung Lee<sup>6</sup>, Andy May<sup>7</sup>, Amy Sullivan<sup>7</sup>, and Sonia M. Kreidenweis<sup>7</sup> (<sup>1</sup>University of Montana; <sup>2</sup>Pacific Northwest National Lab; <sup>3</sup>United States Forest Service; <sup>4</sup>Droplet Measurement Technologies; <sup>5</sup>University of Manchester; <sup>6</sup>Hankuk University of Foreign Studies, Korea; <sup>7</sup>Colorado State University).
5. **The physical properties of black carbon and other light-absorbing material emitted from prescribed fires in the US.** Extended abstract # 129, presented at the Air & Waste Management Association Conference on Aerosol/Atmospheric Optics: Visibility And Air Pollution, September 24-28, 2012, Whitefish, MT. Authors: Gavin R. McMeeking, Sonia M. Kreidenweis, Amy P. Sullivan, Taehyoung Lee, Jeffrey Collett, Jr. (Dept. of Atmospheric Science, Colorado State University, Fort Collins, CO 80523); Robert J. Yokelson, Sheryl Akagi (Dept. of Chemistry and Biochemistry, University of Montana, Missoula, MT 59812); Edward Fortner, Timothy Onasch (Aerodyne Research Inc., Billerica, MA 01821); Jonathan W. Taylor, Hugh Coe (Centre for Atmospheric Science, University of Manchester, Manchester, M13 9PL, UK).
6. **Investigation of Airborne-Based Smoke Marker Ratios from Prescribed Burning.** Submitted for presentation at the Fall Annual Meeting of the American Geophysical Union, December 3-7, 2012, San Francisco, CA. Authors: A.P. Sullivan, S.M. Kreidenweis, Robert J. Yokelson, and J.L. Collett, Jr. (Colorado State University, Department of Atmospheric Science, Fort Collins, Colorado 80523; and University of Montana, Department of Chemistry, Missoula, Montana 59812).

7. **Airborne-Based Carbon Aerosol Observations from Prescribed Burning.** Submitted for presentation at the Fourth Fire Behavior and Fuels Conference, February 18-20, 2013, Raleigh, North Carolina. Authors: A.P. Sullivan<sup>1</sup>, G.R. McMeeking<sup>1</sup>, T. Lee<sup>1</sup>, J.L. Collett, Jr.<sup>1</sup>, Robert J. Yokelson<sup>2</sup>, and S.M. Kreidenweis<sup>1</sup> (<sup>1</sup>Colorado State University, Department of Atmospheric Science, Fort Collins, Colorado 80523; <sup>2</sup>University of Montana, Department of Chemistry, Missoula, Montana 59812).

*PI Kreidenweis organized a Biomass Burning Symposium at the 33rd Annual Meeting of the American Association for Aerosol Research in October, 2014. The following talks acknowledging this project were presented.*

8. **Smoke Marker Ratios from Controlled Laboratory Burns, Prescribed Burns, and Wildfires.** AMY P. SULLIVAN, Sonia Kreidenweis, Bret Schichtel, Jeffrey Collett.
9. **Investigation of Chemical and Physical Perturbations to Organic Aerosol Present in Biomass Burning Plumes over Prescribed Fires in South Carolina.** ANDREW MAY, Taehyoung Lee, Gavin McMeeking, Sheryl K. Akagi, Amy P. Sullivan, Shawn P. Urbanski, Robert J. Yokelson, Sonia Kreidenweis.

*The following talk will be presented at the Fall Meeting of the AGU in December 2014.*

10. A43J-04 **Biomass Burning: Major Uncertainties, Advances, and Opportunities.** Robert J Yokelson<sup>1</sup>, Chelsea Stockwell<sup>2</sup>, Patrick R Veres<sup>3</sup>, Lindsay E Hatch<sup>4</sup>, Kelley C Barsanti<sup>4</sup>, Xiaoxi Liu<sup>5</sup>, Greg Huey<sup>6</sup>, Thomas B Ryerson<sup>3</sup>, Jack E Dibb<sup>7</sup>, Armin Wisthaler<sup>8</sup>, Markus Müller<sup>9</sup>, Matthew James Alvarado<sup>10</sup>, Sonia M Kreidenweis<sup>11</sup>, Allen L Robinson<sup>12</sup>, Owen B Toon<sup>13</sup>, Jeff Peischl<sup>14</sup> and Ilana B Pollack<sup>15</sup>, (1)Univ Montana, Missoula, MT, United States, (2)University of Montana, Missoula, MT, United States, (3)NOAA Boulder, Boulder, CO, United States, (4)Portland State University, Portland, OR, United States, (5)Georgia Institute of Technology, Atlanta, GA, United States, (6)Georgia Institute of Technology Main Campus, School of Earth and Atmospheric Sciences, Atlanta, GA, United States, (7)Univ New Hampshire, Durham, NH, United States, (8)University of Oslo, Department of Chemistry, Oslo, Norway, (9)University of Innsbruck, Innsbruck, Austria, (10)AER, Inc., Lexington, MA, United States, (11)Colorado State Univ, Fort Collins, CO, United States, (12)Carnegie Mellon University, Department of Mechanical Engineering, Pittsburgh, PA, United States, (13)University of Colorado at Boulder, Boulder, CO, United States, (14)NOAA ESRL Chemical Sciences Division, Boulder, CO, United States, Boulder, CO, United States, (15)NOAA, Boulder, CO, United States.

### IV.g.3. Workshops and Meetings

- JFSP Smoke Science Plan (SSP) Science Status Workshop, Fort Collins CO, October, 2014

## V. Management Implications

Findings from this project provided observational evidence of postulated aging mechanisms in biomass burning plumes. They also provided observational tests of the applicability of emission factors developed using data from laboratory studies. Key management implications of findings include the following:

- Emission inventories for primary particles, especially black carbon, and secondary particle precursors that were refined via field observations in this study will improve the ability of air quality modelers to assess the overall impacts of wild and prescribed fires on fine particle concentrations. These findings can be used in models by air quality regulators in developing regional haze and PM<sub>2.5</sub> State Implementation Plans (SIPs) to reduce the haze and PM<sub>2.5</sub> below regulated thresholds.
- The volatile nature of primary particles emitted by biomass burning was observed in this study. Air quality models attempting to represent near-field concentrations of fine particles in a diluting plume thus need to actively treat gas-particle partitioning. Our observational data showed that a large portion of the organic matter present in fine particles in a highly concentrated plume near the source will volatilize and repartition to the gas phase as the plume dilutes. [Note: this implication was also listed in the Final Report for 09-1-3-01, which focused on similar findings from lab studies that were confirmed in our field study.]
- In earlier work, effective and practical techniques for measuring concentrations of chemical species that are tracers of primary particle emissions from biomass burning (e.g., levoglucosan) were reported. The ability to routinely monitor for smoke tracer compounds offers the air quality and fire management communities important new capabilities for identifying the total effect of wild and prescribed fires on regional fine particle concentrations. Our work showed that at least one set of tracer ratios was conserved for several hours after emission, and thus was useful for source apportionment in the near field.

## VI. Relationship to Other Recent Findings and Ongoing Work on This Topic

Emissions from prescribed and wild fires impact air quality and climate on a range of scales, both via direct emissions and via products formed during transport and aging of emissions, including ozone and secondary organic aerosol (SOA). Prior laboratory work that the PIs have been involved in and that has been funded by JFSP, USEPA, and NPS has focused on improved understanding of primary emissions from biomass burning. Through a series of Fire Lab at Missoula Experiments (FLAME), a wide range of biomass fuel types relevant to U.S. prescribed and wild fires were combusted and their emissions characterized. Special emphasis has been placed on emissions of levoglucosan and other smoke marker species to assist in source apportionment studies, emissions of black carbon to understand their radiative and health

impacts, emissions of organic carbon aerosol including characterizing its volatility distribution, and emissions of trace gas species that contribute to ozone and SOA formation.

Recently, in JFSP 09-1-03-1, focus shifted from direct emissions to the secondary effects. On a regional scale, work in the air quality modeling community has shown that models underestimate atmospheric concentrations of organic aerosol, likely due to poor representation of SOA formation mechanisms and the lack of full understanding of source emissions. Among other objectives, that project examined the aging of emissions and the formation of SOA via smog chamber experiments in FLAME III. That study concluded that aged biomass burning aerosol always showed evidence of increased oxidation and for all the experiments combined, the average mass enhancement (the ratio of final aged aerosol mass to direct emissions) was always greater than 1. However, amounts of SOA formed varied greatly across fuel type, including observed mass enhancements less than 1 (i.e., net loss of aerosol during photochemical processing).

The field study work supported by this project and reported herein complements the extensive prior laboratory studies as well as contributing to a series of field studies supported by SERDP. Our study focused on the southeastern U.S., a region with large annual biomass burning activity; prior lab work studied many of the commonly-burned fuels from this region. Our measurements permitted a comparison of observationally-derived emission factors to those measured in the laboratory. For black carbon, a particular focus of this project, we confirmed the utility of the lab studies in the development of emissions databases, although the new online, single-particle measurement technique we employed appears to indicate somewhat higher emissions than did earlier studies using filter-based measurements. For organic aerosol, we confirmed its semivolatile nature and suggested that the evolution of smoke aerosol in the atmosphere within a few hours of emission may be largely driven by physical changes, namely preferential evaporation that leaves the more oxygenated species remaining in the aerosol phase. We also contributed to the ongoing studies of the atmospheric fate of smoke markers, needed to understand how to best use marker species to perform robust apportionment studies.

Finally, the rapid formation of ozone in the plumes we probed indicates a robust photochemistry that points to the importance of the surrounding environment (e.g., NO<sub>x</sub> levels) and may involve the volatilized organic compounds. The production of ozone was higher than observed in fieldwork from the same platform but in different regions, e.g., in California chaparral fire emissions. We could not confirm SOA production in our plumes over the several hours of aging that we could follow with our airborne laboratory, but cannot rule out that the active chemical environment during our study would support production of oxidized condensable (SOA) species, perhaps on longer time scales. A full understanding of the mechanisms of SOA formation and why fuel-to-fuel differences are observed is still lacking. Two newly-funded JFSP studies, 14-1-03-26 and 14-1-03-44, are focused on characterizing SOA precursors and formation mechanisms to shed light on this outstanding question.

## VII. Future Work Needed

To improve confidence in our ability to determine the effects of biomass burning on U.S. air quality, future work that still needs to be addressed includes the following:

- Additional lab and field studies of OA and levoglucosan volatilization and oxidation are needed to develop an improved understanding of the competition between physical and chemical transformations of emissions, including compounds proposed as smoke markers for apportionment studies.
- As mentioned in the prior section, further work is needed in identifying SOA precursors emitted from fires and their atmospheric reaction mechanisms, in gas, particulate, and aqueous phases.

## VIII. Deliverables Cross-Walk

Deliverable Type	Description	Status
Dataset	Dataset documenting BC and OA measurements in simulated wildfires, with associated PM2.5, WSOC, and smoke marker measurements.	Complete. Tabulated data have been provided in the journal articles arising from this project. Data are also available upon request from project PI.
Conference presentations	Invited and contributed presentations at national scientific conferences.	Complete. Numerous invited and contributed presentations have been made at national and international conferences and workshops.
Refereed publication	~3 journal manuscripts describing BC/OA; smoke marker profiles; integrated field study analyses	Nearly complete. Three articles have been published. A fourth article will be submitted in 2014.
Website	Project website reporting results	With increased public availability of project information posted on the JFSP website, we did not create a separate website specifically for this project.
Annual and final reports	Project final report, summarizing results and deliverables	Complete